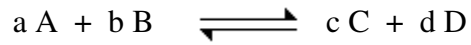


Chemical Equilibrium

Chemical Reaction



Or

$$0 = - a A - b B + c C + d D$$

Or, Formally

$$0 = \sum_i \nu_i J_i$$

A, B, C, D are Chemical Species
a, b, c, d are Stoichiometric Coefficients

J_i are Chemical Species
 ν_i are Stoichiometric Coefficients

Description of Reaction Progress

$$n_i = n_i^\circ + \nu_i \xi$$

n_i is the number of moles of J_i
 n_i° is the initial number of moles of J_i
 ξ is the Reaction Advancement

At Equilibrium

$$n_{i,e} = n_i^\circ + \nu_i \xi_e$$

Condition of Equilibrium

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \Delta G = \sum_i \nu_i \mu_i$$

At Equilibrium

$$\Delta G = 0$$

Equilibrium Constants

$$\Delta G^\circ = -RT \ln(K)$$

$$K = \prod a_i^{\nu_i}$$

Ideal Gases

$$K_P = \prod \left(\frac{P_i}{P^\circ} \right)^{\nu_i} = \prod P_i^{\nu_i}$$

P° is 1 bar or 1 atm, depending on the Table

$$= K_x P^{\Delta \nu}$$

P must be in the same units as P°

$$= K_c (RT)^{\Delta \nu}$$

c must be in units of mol/L

Real Gases

$$K = \prod \left(\frac{f_i}{P^\circ} \right)^{\nu_i} = K_\gamma K_P \\ = \prod \gamma_i^{\nu_i} \prod P_i^{\nu_i}$$

Condensed Phase Solutions

$$K = \prod a_i^{\nu_i} = K_\gamma K_x \\ = \prod \gamma_i^{\nu_i} \prod x_i^{\nu_i}$$

$a_i = \gamma_i x_i$; μ^* reference state

$$= K_\gamma K_x \\ = \prod \gamma_i^{\nu_i} \prod x_i^{\nu_i}$$

$a_i = \gamma_i x_i$; μ^{**} reference state

$$= K_\gamma K_m \\ = \prod \gamma_i^{\nu_i} \prod \left(\frac{m_i}{m^\circ} \right)^{\nu_i}$$

$a_i = \gamma_i m_i/m^\circ$; μ^{***} reference state

$$= K_\gamma K_c \\ = \prod \gamma_i^{\nu_i} \prod \left(\frac{c_i}{c^\circ} \right)^{\nu_i}$$

$a_i = \gamma_i c_i/c^\circ$; μ^\square reference state

Temperature Dependence of K

$$\begin{aligned}\ln K(T) &= \ln K(T_0) - \int_{T_0}^T \frac{\Delta H^0}{R} d\left(\frac{1}{T}\right) \\ &= \ln K(T_0) - \frac{\Delta H^0}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\end{aligned}$$

Assumes ΔH^0 is constant

Le Chatelier's Principle

$$0 = -\frac{\Delta H}{T} dT_e + \Delta V dP_e + G_e'' d\xi_e$$

$$G_e'' = \left(\frac{\partial^2 G}{\partial \xi^2}\right) > 0$$

Constant P

$$\left(\frac{\partial \xi_e}{\partial T}\right)_P = \frac{\Delta H}{T G_e''}$$

Constant T

$$\left(\frac{\partial \xi_e}{\partial P}\right)_T = -\frac{\Delta V}{G_e''}$$